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Modeling the effect of solvent on the possibility of the formation the HSO_3^+ cation

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Abstract

The possibility of describing the reactions of heterolytic dissociation sulfuric acid and the further conversion of the $H_3SO_4^+$ cation to HSO_3^+ by the density functional theory method was studied. By comparing with the calculated and experimental data, a functional and a basic set were selected for modeling these reactions.

The influence of the solvent on the course of the studied reactions was studied: based on COSMO continuum model (implicit solvent accounting) and explicit solvent accounting (introduction of particles participating in the reaction into the solvation shell of four sulfuric acid molecules). It was shown that individually neither the continuum model nor the explicit solvent accounting can adequately describe the reactions under study from the aspect of energy effects.

It was determined that the reactions studied can occur only in strongly polar solvents. The effect of the content of sulfuric trioxide in oleum on the particle formation energy of $H_3SO_4^+$ and HSO_3^+ was studied. It was shown that an increase in the concentration of sulfuric trioxide from 0 to 15% reduces the energy spent on the formation of $H_3SO_4^+$ and HSO_3^+ particles by 2.5 and 3.5 kJ/mol, which leads to an increase in the equilibrium constants of the formation reactions of these products by 2.74 and 4.11 times.

An approximate estimate is made of the equilibrium constant of the reaction of formation of the HSO_3^+ cation, equal to $\sim 10^{-7}$-10^{-8}.

It was shown that particles of HSO_3^+ and SO_3 in sulfuric acid solutions exist in the form of associates with sulfuric acid, through the sulfur atom SO_3/HSO_3^+ and oxygen H_2SO_4, in which the S···O distance is 1.98 Å for SO_3 and 1.9 Å for HSO_3^+.

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